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Quartz Crystal Microbalance Studies: Solvent Effects in Conducting Polymer Films

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Introduction

The use of the Quartz Crystal Microbalance (QCM) makes possible in-situ measurements of mass change occurring during oxidation/reduction of electroactive polymer films. For films which exhibit "ideal" behavior in specific electrolyte solutions, i.e., polyvinylferrocene (PVF) in $LiClO_4$/acetonitrile, it is possible to measure solvent swelling/shrinkage effects during cycling. An ideal film has the following properties:

Reversibility: The oxidation/reduction process causes no loss of charge capacity and anions/cations are inserted/removed reversibly with no change in the electroactivity of the film.

Cation or anion only is inserted to maintain electroneutrality: There is no "mixed"nature of counterion insertion so prediction of mass change due to the weight of inserted counterion is possible.

Since we can predict the ideal mass change due to counterion insertion from charge data obtained during cycling, deviations can be attributed to solvent addition or removal during the cycling process. The movement of solvent may be due to solvated counterion movement or to film expansion or contraction causing a net volume change during oxidation/reduction.

Experimental

Gold coated crystals were obtained from Inficon (East Syracuse, N.Y.). These were shear mode (6MHz) crystals with a surface area of 0.33 cm^2 coated with electroactive polymer exposed to the electrolyte solution. Films were prepared by spin-coating the crystals with a solution of 0.4 mg/ml PVF in methylene chloride, at 200-300 rpm for 10 sec. The resulting films were around 2000-4000 Å in thickness. Cycling of the films produced a frequency shift of around 2000 Hz, due to counterion and solvent motion. The frequency shift was measured with a frequency counter (HP5384A) and stored in a personal computer (HP9816). The crystal oscillator circuit included a power source and an oscillator (Inficon XTC).

The experiments were performed in a 4-necked glass cell. Two of the necks were used for gas inlet/outlet and one for the reference electrode (SCE) and the last for the counterelectrode (large area platinum). The working electrode was the polymer/gold/quartz attached to the open tube in the bottom of the cell with a silicone sealant.

The electrode potential was controlled by a potentiostat (EG&G PAR 173). The working electrode was grounded through the potentiostat and the oscillator was connected to the circuit through a 1 µF capacitor in series.

The polymer film was treated as rigid since the film thickness was small compared to the thickness of the crystal. The Sauerbrey equation was used to analyze the data:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_\Omega \mu_\Omega}} \frac{\Delta m}{A}$$

Results and Discussion

Polyvinylferrocene exhibits ideal reversible behavior in perchlorate electrolyte in either acetonitrile or water. For films inserting only anions, a plot of E_{peak} vs. electrolyte concentration should have a slope of -59 mv/decade, which is seen in these systems (fig.1). Since the exact weight of counterion can then be predicted from charge data taken during oxidation/reduction, any deviations in actual mass measured by QCM are attributed to solvent movement.

For perchlorate/acetonitrile solvents, oxidation of PVF caused insertion of 1 ClO_4^- and 0.25 AN per PVF electroactive site. Reduction processes are exactly reversible, so that 1 ClO_4^- + 0.25 AN per site are removed during the cathodic sweep. If a small amount of cation were being released from the film during oxidation, the observed deviation would be a measurement of a smaller mass change than expected rather than a larger one. For PVF oxidation in aqueous solution, insertion of 1 ClO_4^- with the simultaneous exclusion of 0.4 H_2O per electroactive PVF site occurs. This process is again exactly reversible so that reduction

removes 1 ClO_4^- and reinserts 0.4 H_2O (fig.2). In this case, it is possible that PVF is acting in a slightly non-ideal manner and that the observed deviation (being less than that expected) is actually caused by cation movement out of the film along with anion insertion during the oxidative sweep.

The authors intend to discuss possible mechanisms for observed solvent effects in pure and mixed solvents. Mixtures should result in intermediate behavior between inclusion (pure acetonitrile) and exclusion (pure H_2O) during the oxidation scan.

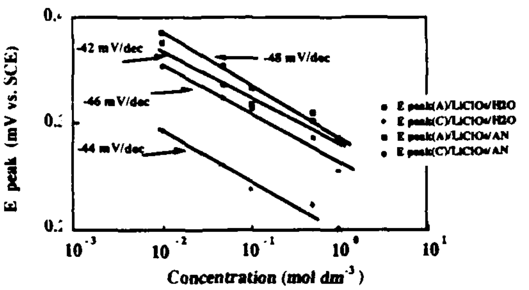

Fig.1 E_{peak} plotted vs. electrolyte concentration for $LiClO_4$ salt in acetonitrile and water. Observed slopes are close to the predicted value of -59 mV/decade for systems inserting only anions.

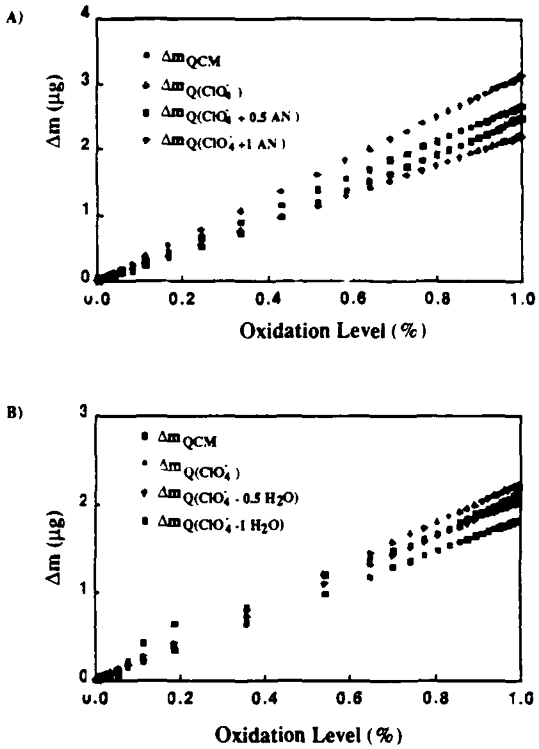

Fig.2 Mass change vs. oxidation state for perchlorate electrolyte in A) acetonitrile and B) water. Comparison of actual mass change vs. mass change predicted for perchlorate movement (from charge data) shows amount of solvent movement.

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